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[Title of the Invention]

LITHIUM MANGANATE PARTICULATE COMPOSITION AND A METHOD FOR PRODUCING
THE SAME AND A LITHIUM ION RECHARGEABLE BATTERY

[Abstract] (With amendment)

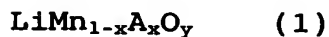
[Problem to be Solved]

The present invention provides a particulate composition, which is favorable as a powder for a positive active material for a rechargeable lithium ion battery, has a narrow particle size distribution, a large specific surface area, and a homogeneous

composition, a method for producing the same, as well as a rechargeable lithium ion battery produced using the same.

[Solution]

The present invention is a particulate composition consisting of secondary particles that are primary particles aggregated together, wherein the primary particle is represented by the formula (1);



(wherein x represents a rational number between 0 and 0.25. y represents a rational number between 1.875 and 2.25. A is selected from the group consisting of B, Mg, Al, Si, Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ru, Sn, Sb, La, Ce, Pr, Nd, Hf, Ta, and Pb.), is essentially spherical, the average particle size is 0.1 to 5 μm , the secondary particles are essentially spherical, the average particle size is 1 to 100 μm , and the specific surface area is 0.1 to 10 m^2/g .

[Claims for the Patent]

[Claim 1]

A particulate composition consisting of secondary particles that are primary particles aggregated together, characterized in that said primary particle consists of lithium manganese complex oxide represented by the following general formula (1);



(wherein x represents a rational number between 0 and 0.25. y represents a rational number between 1.875 and 2.25. A represents at least one element selected from the group consisting of B, Mg, Al, Si, Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ru, Sn, Sb, La, Ce, Pr, Nd, Hf, Ta, and Pb.), said primary particles are

essentially spherical, the average particle size of said primary particles is 0.1 to 5 μm , said secondary particles are essentially spherical, the average particle size of said secondary particles is 1 to 100 μm , and the specific surface area of said secondary particles is 0.1 to 10 m^2/g .

[Claim 2]

A method for producing the particulate composition according to claim 1 comprising dispersing a particulate composition consisting of manganese oxyhydroxide in an aqueous lithium hydroxide solution, and then performing a heating process, characterized in that said particulate composition consisting of manganese oxyhydroxide is a particulate composition consisting of secondary particles that are primary particles aggregated together, said primary particle consists of manganese oxyhydroxide represented by the following general formula (2);



(wherein x represents a rational number between 0 and 0.25, y represents a rational number between 1.875 and 2.25. A represents at least one element selected from the group consisting of B, Mg, Al, Si, Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ru, Sn, Sb, La, Ce, Pr, Nd, Hf, Ta, and Pb.), and said particulate composition consisting of manganese oxyhydroxide comprises at least one element selected from the group consisting of B, Mg, Al, Si, Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ru, Sn, Sb, La, Ce, Pr, Nd, Hf, Ta, and Pb in an amount of 0 to 1/3 g atom per 1 g atom of manganese.

[Claim 3]

The method for producing the particulate composition according to claim 2, wherein the concentration of the particulate composition

consisting of manganese oxyhydroxide dispersed in the aqueous lithium hydroxide solution is 0.05 to 10 mol/L.

[Claim 4]

The method for producing the particulate composition according to claim 2 or 3, wherein the molar ratio of lithium hydroxide and manganese oxyhydroxide is (lithium hydroxide)/(manganese oxyhydroxide) = 1/1 to 20/1.

[Claim 5]

The method for producing the particulate composition according to claim 2, 3, or 4, wherein the temperature of the heating process is 100 to 215°C.

[Claim 6]

The method for producing the particulate composition according to claim 1, characterized in that the particulate composition obtained according to claim 2, 3, 4, or 5 is further subjected to a dry calcination process.

[Claim 7]

A rechargeable lithium ion battery characterized in that the particulate composition according to claim 1 is used as a positive active material.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a particulate composition which can be used as a raw material for a positive active material of a rechargeable lithium ion battery, a novel method for producing the same, and a rechargeable lithium ion battery produced using the same.

[0002]

[Conventional Art]

Lithium manganese complex oxide is one of the materials recently noted as a positive active material used in a rechargeable lithium ion battery that is used as a high power and high energy density battery in, for example, a notebook sized personal computer, a PHS, and a cellular phone. This, as described in for example "Cho-Onpa Fummu Bunkai Hou Ni Yoru Kyu-jou LiCoO₂ Bifuntai No Gousei To Ritiumu Niji Denchi You Kassei Busshitu He No Ouyou (Synthesis of Spherical LiCoO₂ Micropowder by Ultrasonic Atomization Decomposition Method and Application to Active Material for Lithium Rechargeable Battery)" (Takashi Ogiwara, Yoshihiko Saito, Teruaki Yanagawa, Nobuo Ogata, Kokichi Yoshida, Masayuki Takashima, Susumu Yonezawa, Yasuharu Mizuno, Norifumi Nagata, Kenji Ogawa; Journal of the Ceramic Society of Japan, Vol. 101, p. 1159 to 1163 (1993) (hereinafter referred to as "Reference 1".)), belongs to a group of compounds represented by LiMO₂ (wherein M represents Cr, Mn, Ni, Fe, Co or V.), and it has among those a particular high charge voltage among these along with LiCoO₂. It is therefore extremely favorable as a positive active material. Among these, LiMnO₂ is thought to be advantageous in cost because it uses manganese that is both abundant and inexpensive as a resource.

[0003]

As methods for producing LiMnO₂, Japanese Patent Laid-Open No. 5-242889 discloses a method of blending Li₂MnO₃ and MnO at an equimolar amount and calcinating in an inert gas, and a method of blending LiOH and MnOOH at an equimolar amount and calcinating in an inert gas. These methods, however, are capable of synthesis only in an atmosphere without oxygen such as in N₂ stream, and it was necessary to limit the atmosphere for synthesis.

[0004]

Tabuchi et al., Solid State, vol. 89, p. 53-63 (1996) describes a method for obtaining LiMnO_2 by performing a hydrothermal reaction of LiOH and MnOOH under a large excess of LiOH . This method, however, is capable of providing a LiMnO_2 haploid only under a large excess of LiOH such that an Li/Mn ratio of feed is 50, and therefore had problems in terms of economic efficiency and operability.

[0005]

Japanese Patent Laid-Open No. 7-101728 discloses a layered LiMnO_2 consisting of particles with a particle size of $5\text{ }\mu\text{m}$ or less and having a BET specific surface area of $10\text{ m}^2/\text{g}$ or more, and a production method thereof. However, because this material merely regulates the particle size, the particles aggregate and dispersibility was not good. It therefore had a drawback that high density packing was difficult in a battery for practical use.

[0006]

In the meantime, when a powder is used as a positive active material of a rechargeable lithium ion battery, as described in for example Reference 1, p. 1159, in order to obtain high reliability and reproducibility in terms of properties such as stability against the negative electrode, internal resistance, sensitivity, and response speed during charge and discharge, it is necessary to pack a powder with narrow particle size distribution and which is a homogeneous composition at high density. Especially in a battery for practical use, the volume in which the powder can be packed is constant. Accordingly, if there was no difference in the battery performance per unit weight of the positive active material, more electrical quantity can be retrieved with higher packing property and larger

specific surface area of the powder. It is therefore of extreme importance that the powder has high packing property and large specific surface area, when producing a rechargeable lithium ion battery having high reliability and reproducibility to various properties as well as high power.

[0007]

In all of the above-described lithium manganese complex oxides, however, the primary particle aggregates and dispersibility is poor. It was therefore difficult to pack at a high density for a battery for practical use.

[0008]

Among methods commonly used for producing LiMnO_2 is a method by calcination. European Published Patent No. 736918A1 discloses that LiMnO_2 having a particle size of 1 to 100 μm is favorable as a positive electrode material for a rechargeable battery. Solid State Ionics, vol. 89 (1996) p. 127 to 137 discloses a technique for synthesizing LiMnO_2 by calcinating a mixture of LiOH and Mn_2O_3 , Table-1 of which discloses a material having 1 to 10 μm and specific surface area 0.51 to 0.77 m^2/g . Japanese Patent Laid-Open No. 8-37027 discloses a technique for producing LiMnO_2 by calcinating LiOH with $\delta\text{-MnOOH}$ or LiOH with Mn_2O_3 .

[0009]

LiMnO_2 produced by such calcination, however, requires grinding after production, and because the ground particles are not essentially spherical particles, it has drawbacks in that the packing property was poor and charge and discharge capacity decreases.

[0010]

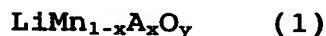
[Problems to be Solved by the Invention]

In light of the above, the object of the present invention is to provide a particulate composition that is favorable as a powder for a positive active material for a rechargeable lithium ion battery, having a narrow particle size distribution and a large specific surface area, and that is a homogeneous composition, a method for producing the same, as well as a rechargeable lithium ion battery produced using the same.

[0011]

[Means for Solving the Problems]

The present invention is a particulate composition consisting of secondary particles that are primary particles aggregated together, wherein the above primary particle consists of lithium manganese complex oxide represented by the following general formula (1);



(wherein x represents a rational number between 0 and 0.25. y represents a rational number between 1.875 and 2.25. A represents at least one element selected from the group consisting of B, Mg, Al, Si, Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ru, Sn, Sb, La, Ce, Pr, Nd, Hf, Ta, and Pb.), wherein the above primary particles are essentially spherical, the average particle size of the above primary particles is 0.1 to 5 μm , the above secondary particles are essentially spherical, the average particle size of the above secondary particles is 1 to 100 μm , and the specific surface area of the above secondary particles is 0.1 to 10 m^2/g . The present invention is also a method for manufacturing the particulate composition, wherein a particulate composition consisting of manganese oxyhydroxide is dispersed in an aqueous lithium hydroxide solution, and then heated. The present invention is further a rechargeable

lithium ion battery produced using the above particulate composition as the positive active material. The present invention is described in detail below.

[0012]

The particulate composition of the present invention consists of lithium manganese complex oxide represented by the above general formula (1). The above x is a rational number between 0 and 0.25. The above y is a rational number between 1.875 and 2.25. y assumes a value within the above range according to the valence of element A and the value of x .

[0013]

The particulate composition of the present invention may consist of lithium manganese complex oxide having the composition represented by LiMnO_2 which corresponds to the above general formula (1) wherein $x = 0$ and $y = 2$, or it may consist of lithium manganese complex oxide having the composition corresponding to the above general formula (1) wherein $0 < x \leq 0.25$ and $1.875 \leq y \leq 2.25$.

[0014]

When the particulate composition of the present invention consists of lithium manganese complex oxide having the composition corresponding to the above general formula (1) wherein $0 < x \leq 0.25$ and $1.875 \leq y \leq 2.25$, it can comprise in addition to atom Mn at least one atom selected from the group consisting of B, Mg, Al, Si, Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ru, Sn, Sb, La, Ce, Pr, Nd, Hf, Ta, and Pb.

[0015]

In the above general formula (1), examples of lithium manganese complex oxides having the composition corresponding to $0 < x \leq 0.25$

and $1.875 \leq y \leq 2.25$ include $\text{LiMn}_{0.9}\text{Co}_{0.1}\text{O}_2$, $\text{LiMn}_{0.95}\text{V}_{0.05}\text{O}_{2.05}$, $\text{LiMn}_{0.98}\text{V}_{0.02}\text{O}_{2.02}$, $\text{LiMn}_{0.85}\text{Fe}_{0.15}\text{O}_2$, $\text{LiMn}_{0.95}\text{Ni}_{0.05}\text{O}_2$, $\text{LiMn}_{0.97}\text{Ti}_{0.03}\text{O}_{2.015}$, $\text{LiMn}_{0.97}\text{Cu}_{0.03}\text{O}_{1.985}$, $\text{LiMn}_{0.98}\text{Sb}_{0.02}\text{O}_{2.02}$, $\text{LiMn}_{0.90}\text{B}_{0.10}\text{O}_2$, $\text{LiMn}_{0.95}\text{Mg}_{0.05}\text{O}_{1.975}$, $\text{LiMn}_{0.80}\text{Fe}_{0.20}\text{O}_2$, and $\text{LiMn}_{0.99}\text{Ta}_{0.01}\text{O}_2$.

[0016]

The crystal structure of the above lithiummanganese complex oxide is an orthorhombic crystal, and its X-ray diffraction pattern is similar to that of LiMnO_2 described in No. 35-749 of JCPDS (Joint Committee Powder Diffraction Standards) card.

[0017]

In the particulate composition of the present invention, the above primary particles are essentially spherical, and the average particle size of the above primary particles is 0.1 to 5 μm . "Essentially spherical" as used herein refers to a particle having properties identical to a particle observed as a sphere under a microscope and having physical properties determined to be a sphere, even if its shape is actually layered. If the average particle size of the above primary particles is less than 0.1 μm , when it is used as a positive active material of a rechargeable lithium ion battery, packing rate will decrease and therefore electric capacity per unit volume of the battery will decrease. If the average particle size of the above primary particles is greater than 5 μm , when it is used as a positive active material of a rechargeable lithium ion battery, electric capacity will be inadequate. The average particle size is therefore limited to the above range, preferably 0.2 to 3 μm .

[0018]

In the particulate composition of the present invention, the above primary particles that are the above primary particles aggregated

together are essentially spherical, the average particle size of the above secondary particles is 1 to 100 μm , and the specific surface area of the above secondary particles is 0.1 to 10 m^2/g . If the average particle size of the above secondary particles is less than 1 μm , when it is used as a positive active material of a rechargeable lithium ion battery, a packing rate will decrease and therefore electric capacity per unit volume of the battery will decrease. If the average particle size of the above secondary particles is greater than 100 μm , its particle may penetrate a separator consisting of a polymer film such as polypropylene which separates the negative and positive electrodes and produce a short circuit. The average particle size is therefore limited to the above range, preferably 1 to 30 μm . If the specific surface area of the above secondary particles is less than 0.1 m^2/g , the specific surface area will be too small, and when it is used as a positive active material of a rechargeable lithium ion battery, large amounts of electrical quantity cannot be retrieved quickly. If the specific surface area of the above secondary particles is greater than 10 m^2/g , problems regarding stability and safety may arise. The specific surface area is therefore limited to the above range, preferably 0.1 to 5 m^2/g .

[0019]

Because the average particle size of the above primary particles of the particulate composition of the present invention is within the above range, high reliability and reproducibility can be obtained in terms of properties such as stability against the negative electrode, internal resistance, sensitivity, and response speed during charge and discharge, when used as a positive active material of a rechargeable lithium ion battery. Moreover, because the average particle size of

the above secondary particles is within the above range, when it is used as a positive active material of a rechargeable lithium ion battery, the packing and the electric capacity per unit volume of the battery that can be obtained will be high, and the specific surface area of the above aggregated particle will be within the above range. Accordingly, when it is used as a positive active material of a rechargeable lithium ion battery, a large electrical quantity can be stably retrieved.

[0020]

In the present invention, a particulate composition consisting of lithium manganese complex oxide can be produced by dispersing a particulate composition consisting of manganese oxyhydroxide in an aqueous lithium hydroxide solution, and then performing a heating process.

[0021]

The above manganese oxyhydroxide used in the present invention is not particularly limited, and examples include those for which the average particle size of the secondary particles that are primary particles aggregated together is 1 to 100 μm and which is represented by the following general formula (2);



(wherein x represents a rational number between 0 and 0.25. y represents a rational number between 1.875 and 2.25. A represents at least one element selected from the group consisting of B, Mg, Al, Si, Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ru, Sn, Sb, La, Ce, Pr, Nd, Hf, Ta, and Pb.), and A in the above general formula (2) comprises at least one element selected from the group consisting of B, Mg, Al, Si, Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Ga,

Y, Zr, Nb, Mo, Ru, Sn, Sb, La, Ce, Pr, Nd, Hf, Ta, and Pb in an amount of 0 to 1/3 g atom per 1 g atom of manganese. If the above amount of the at least one element comprised in the above 1 g atom of manganese is greater than 1/3 g, when it is used in a rechargeable lithium ion battery, charge and discharge capacity will remarkably decrease.

[0022]

Manganese oxyhydroxide as defined herein is represented by MnOOH when $x = 0$, and this refers to $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$. In other words, manganese oxyhydroxide is generally referred to manganese sesquioxide (Mn_2O_3) having one molecule of water, although the water molecule may be less than one or one or more. Needless to say, this is also the case when $0 < x \leq 0.25$, which corresponds to the manganese oxyhydroxide according to the present invention. A compound having one water molecule is shown as a representative manganese oxyhydroxide in the above general formula (2), although due to the above reason, it is not limited to this.

[0023]

The above manganese oxyhydroxide can be obtained by for example neutralizing a compound having divalent manganese such as manganese nitrate, manganese chloride, and manganese sulfate with an alkali, and then oxidizing this with an oxidizer such as air, oxygen, and hydrogen peroxide. The method for producing the above manganese oxyhydroxide is not particularly limited, and examples include a method of carbonating an aqueous solution of the above divalent manganese compound or an aqueous mixture of a divalent manganese compound and a compound of element A, treating with an alkali, and then finally treating with an acid. A commercially available manganese oxyhydroxide can also be used.

[0024]

In the production method of the present invention, the above manganese oxyhydroxide is dispersed in the above aqueous lithium hydroxide solution. The above aqueous lithium hydroxide solution comprises lithium and hydroxide ions in an aqueous solution. This can be prepared by dissolving in water a compound that can produce lithium and hydroxide ions in an aqueous solution, for example, lithium hydroxide, lithium oxide, and metal lithium. "Aqueous lithium hydroxide solution" as used herein means a preparation prepared by dissolving in water a compound that can produce lithium and hydroxide ions in the above aqueous solution. In the present invention, a compound that can produce lithium and hydroxide ions in the above aqueous solution is used as the lithium source.

[0025]

The concentration of the above manganese oxyhydroxide in a dispersion is not particularly limited, although 0.05 to 10 mol/L is typically preferred, and more preferably 0.1 to 5 mol/L in regard to operability and economic efficiency in the production process.

[0026]

Because the residual lithium source can be recollected after reaction, the molar ratio of the above aqueous lithium hydroxide solution and the above manganese oxyhydroxide is not particularly limited, provided that $(\text{lithium hydroxide})/(\text{manganese oxyhydroxide}) \geq 1$, and preferably $(\text{lithium hydroxide})/(\text{manganese oxyhydroxide}) = 1/1$ to $20/1$ in regard to operability and economic efficiency in the production process, more preferably $(\text{lithium hydroxide})/(\text{manganese oxyhydroxide}) = 1/1$ to $10/1$, further preferably $(\text{lithium hydroxide})/(\text{manganese oxyhydroxide}) = 1/1$ to $5/1$.

[0027]

In the production method of the present invention, if the molar ratio of the above aqueous lithium hydroxide solution and the above manganese oxyhydroxide is (lithium hydroxide)/(manganese oxyhydroxide) < 1 , the total content of manganese and element A in the particulate composition obtained will be greater than the lithium content.

[0028]

In the production method of the present invention, a particulate composition having the composition corresponding to the above general formula (1) wherein $0 < x \leq 0.25$ can be obtained by further dispersing in the above dispersion a compound consisting of at least one element selected from the group consisting of B, Mg, Al, Si, Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ru, Sn, Sb, La, Ce, Pr, Nd, Hf, Ta, and Pb. The above compound is not particularly limited, and examples include the simple substance, hydroxides, and oxides of the above element. These may be used alone or in combination of two or more. The amount of the above compound added relative to the sum of the manganese atom and the atom of the above element in the above compound can be such that the proportion of the atom of the above element is 0.25 or less in the dispersion as an atomic ratio.

[0029]

In the production method of the present invention, since reactivity will be better when the concentration of the hydroxide ion in the above dispersion is higher, a compound that can produce hydroxide ions can further be added to the above dispersion. The compound that can produce the above hydroxide ions is not particularly

limited, and examples include sodium hydroxide, potassium hydroxide, and ammonium hydroxide.

[0030]

In the present invention, the above particulate composition can be produced by dispersing manganese oxyhydroxide particle powder in an aqueous lithium hydroxide solution, and then performing a heating process. The heating temperature in the above heating process is preferably 100 to 215°C. If the temperature is less than 100°C, a long time is required to complete the reaction, and if the temperature is higher than 215°C, the water vapor pressure will be extremely high and pressure resistance of the reaction container must be maintained, creating a problem in economic efficiency in regard to the cost of equipment. The temperature is preferably 100 to 200°C in regard to operability and economic efficiency in the production process. When the heating temperature is greater than 100°C, a pressure resistance container is used as the reaction container to control boiling of the above water dispersion. The reaction time in the above heating process will vary according to the heating temperature and will be several minutes to several days. The above heating process may be carried out with stirring of the dispersion.

[0031]

In the production method of the present invention, the powdered particulate composition of interest can be obtained by first performing the above heating process, and then cooling the reaction solution to a temperature at which a separation step is possible, separating the precipitate using a separation method such as filtration, sufficiently washing with water, and then drying. Depending on the objective, the composition can be dried without washing with water.

The drying temperature above is not particularly limited, provided that moisture adsorbed to the particulate composition can be sufficiently removed.

[0032]

Moreover, a dry calcination process may be performed with the product after drying as necessary. By performing the above dry calcination process, the crystallinity of the particulate composition obtained can further be increased, and the sizes of the primary and secondary particles can be adjusted. A particulate composition that is in accord with the desired battery properties can thus be obtained. The above dry calcination process can be performed after drying and after collecting the particulate composition obtained, or may be performed simultaneously with the drying process. In addition, the above dry calcination process may be performed in an arbitrarily controlled atmosphere such as air, nitrogen, or argon. The liquid phase separated in the above filtration etc. can either be collected and reused, or discarded after processing.

[0033]

The production method of the present invention differs from the conventional method for producing a particulate composition that uses a solid-phase reaction at a high temperature, in that a particulate composition free from particle sintering and having evenly sized particles can be produced. Accordingly, there is no need for a conventionally performed process of grinding the particles, and a particulate composition with narrow particle size distribution can be obtained.

[0034]

In the production method of the present invention, a particulate composition that is homogeneous in composition and superior in the homogeneity of crystal structures can be obtained. Since the above particulate composition is produced at a lower temperature compared to the solid phase method and produced from a reaction in a dispersed solvent, its specific surface area is maintained at a high value. Moreover, if the compound represented by the above general formula (2), wherein the average particle size of the spherical secondary particles that are primary particles aggregated together is 1 to 100 μm , is used as the raw material for the above manganese oxyhydroxide used in the production method of the present invention, lithium manganese complex oxide superior as a positive active material of a rechargeable lithium ion battery can be obtained.

[0035]

The above positive active material is typically used as a kneaded paste obtained by adding a conduction material, a binder material, and a filler, etc. to the above particulate composition and kneading. The above conduction material is not particularly limited provided that it is an electric conduction raw material that does not cause any chemical change in a rechargeable lithium ion battery, and examples include natural graphite, artificial graphite, carbon black, acetylene black, Ketchen black, carbon fiber, metal powder, metal fiber, and a polyphenylene derivative. These may be used alone or in combination of two or more. The amount of the above conduction material added is not particularly limited. Typically, the amount is preferably 1 to 50% by weight of the above kneaded paste, more preferably 2 to 30% by weight.

[0036]

The above binder material is not particularly limited, and examples include starch, polyvinyl alcohol, carboxymethylcellulose, hydroxypropylcellulose, regenerated cellulose, diacetyl cellulose polyvinyl chloride, polyvinyl pyrrolidone, tetrafluoroethylene, polyvinylidene fluoride, polyethylene, polypropylene, ethylene-propylene-diene copolymer (EPDM), sulfonated EPDM, styrene-butadiene rubber, polybutadiene, fluororubber, and polyethylene oxide. These may be used alone or in combination of two or more. The amount of the above binder material added is not particularly limited. Typically, the amount is preferably 1 to 50% by weight of the above kneaded paste, more preferably 2 to 30% by weight.

[0037]

The above filler is not particularly limited provided that it is a fibrous raw material that does not cause any chemical change in a rechargeable lithium ion battery, and examples include polypropylene, olefin polymer such as polyethylene, glass, and fiber such as carbon. The amount of the above filler added is not particularly limited. Typically, the amount is preferably 0 to 30% by weight of the above kneaded paste.

[0038]

In the rechargeable lithium ion battery of the present invention, the negative electrode raw material is not particularly limited provided that it is typically used in a rechargeable lithium ion battery, and examples include stainless steel, nickel, copper, titanium, aluminum, and calcinated carbon.

[0039]

The rechargeable lithium ion battery of the present invention uses as a positive active material a particulate composition, which is essentially spherical particles that are essentially spherical primary particles aggregated together, wherein the average particle size of the above primary particles is 0.1 to 5 μm , the average particle size of the above secondary particles is 1 to 100 μm , the specific surface area is 0.1 to 10 m^2/g , and having a narrow particle size distribution. High reliability and reproducibility can therefore be obtained in regard to properties such as stability against the negative electrode, internal resistance, sensitivity, response speed during charge and discharge, and electric capacity.

[0040]

The rechargeable lithium ion battery of the present invention can be favorably used in for example electronic equipments such as a notebook sized personal computer, a cellular phone, a cordless handset, a videotape camera recorder, a liquid crystal television, an electric shaver, a portable radio, a headphone stereo cassette tape player, a backup power source, and a memory card; and medical equipments such as a pace maker and a hearing aid.

[0041]

[Examples]

The present invention will now be described in further detail below with Examples. The present invention is not to be limited to these Examples.

[0042]

Example 1

To a slurry of manganese carbonate having an average particle size of secondary particles that were primary particles aggregated

together at 2 μm , a sodium hydroxide solution was added under a nitrogen gas stream, and the manganese hydroxide obtained by neutralization was oxidized in a water slurry with blowing of air, to obtain a manganese oxyhydroxide cake. The average particle size of these secondary particles of manganese oxyhydroxide was 2 μm . To 0.5 mols of the above manganese oxyhydroxide, 10 mol of lithium hydroxide was added, and ion exchanged water was added to this mixture to a total amount of 1 L. This slurry was placed in an autoclave, and hydrothermal processing was performed at a heating process temperature of 100°C and for a heating process duration of 96 hours. The processing conditions of the above process are summarized in Table 1. After the reaction was completed, the slurry was filtrated, washed with water, and dried at 100°C. Subsequent measurement of the X-ray diffraction pattern of the powder obtained confirmed a pattern similar to that of lithium manganese complex oxide. The aggregated particle was confirmed to be spherical by a SEM image observation. The average particle size of the primary particles of the present Example, as well as the shape, the average particle size, the specific surface area, and particle state or the aggregated particle are shown in Table 2.

[0043]

The above average particle size and the above specific surface area were measured by the following methods.

Measurement of Average Particle Size

A photograph was taken using a scanning electron microscope (JSM-840F, manufactured by JEOL Co., Ltd.), arbitrary 200 primary particles were selected from the electron microscope photograph, and

the weighted average of their lengths was set as the average particle size.

Measurement of Specific Surface Area

Measurement was performed using a surface area measuring equipment (Monosorb, manufactured by Quontachrome).

[0044]

Example 2

A manganese oxyhydroxide ($\text{Mn}_{0.90}\text{Co}_{0.10}\text{OOH}$) was obtained as in Example 1, except that a carbonate salt of manganese and cobalt blended at a molar ratio of 0.9 : 0.1 was used. The manganese oxyhydroxide obtained was essentially spherical secondary particles that were primary particles aggregated together, and the average particle size of the secondary particles was 5 μm . One mol of the above manganese oxyhydroxide was blended with 10 mols of lithium hydroxide, and ion exchanged water was added to this mixture to a total amount of 1 L. This slurry was placed in an autoclave, and hydrothermal processing was performed at a heating process temperature of 120°C and for a heating process duration of 48 hours. The processing conditions of the above process are summarized in Table 1. After the reaction was completed, the slurry was filtrated, washed with water, and dried at 100°C. Subsequent measurement of the X-ray diffraction pattern of the powder obtained confirmed a pattern similar to that of lithium manganese complex oxide. Measurements similar to Example 1 were performed, and the results are shown in Table 2.

[0045]

Example 3

A manganese oxyhydroxide ($\text{Mn}_{0.80}\text{Fe}_{0.20}\text{OOH}$) was obtained as in Example 1, except that a carbonate salt of manganese and iron blended

at a molar ratio of 0.8 : 0.2 was used. The manganese oxyhydroxide obtained was essentially spherical secondary particles that were primary particles aggregated together, and the average particle size of the secondary particles was 10 μm . One mol of the above manganese oxyhydroxide was blended with 5 mols of lithium hydroxide, and ion exchanged water was added to this mixture to a total amount of 1 L. This slurry was placed in an autoclave, and hydrothermal processing was performed at a heating process temperature of 150°C and for a heating process duration of 24 hours. The processing conditions of the above process are summarized in Table 1. After the reaction was completed, the slurry was filtrated, washed with water, and dried at 100°C. Subsequent measurement of the X-ray diffraction pattern of the powder obtained confirmed a pattern similar to that of lithium manganese complex oxide. Measurements similar to Example 1 were performed, and the results are shown in Table 2.

[0046]

Example 4

A manganese oxyhydroxide ($\text{Mn}_{0.95}\text{Ni}_{0.05}\text{OOH}$) was obtained as in Example 1, except that a carbonate salt of manganese and nickel blended at a molar ratio of 0.95 : 0.05 was used. The manganese oxyhydroxide obtained was essentially spherical secondary particles that were primary particles aggregated together, and the average particle size of the secondary particles was 10 μm . Three mols of the above manganese oxyhydroxide were blended with 6 mols of lithium hydroxide, and ion exchanged water was added to this mixture to a total amount of 1 L. This slurry was placed in an autoclave, and hydrothermal processing was performed at a heating process temperature of 200°C and for a heating process duration of 4 hours. The processing conditions of the above

process are summarized in Table 1. After the reaction was completed, the slurry was filtrated, washed with water, and dried at 100°C. Subsequent measurement of the X-ray diffraction pattern of the powder obtained confirmed a pattern similar to that of lithium manganese complex oxide. Measurements similar to Example 1 were performed, and the results are shown in Table 2.

[0047]

Example 5

A manganese oxyhydroxide ($\text{Mn}_{0.98}\text{V}_{0.02}\text{OOH}$) was obtained as in Example 1, except that a carbonate salt of manganese and vanadium blended at a molar ratio of 0.98 : 0.02 was used. The manganese oxyhydroxide obtained was essentially a spherical aggregated manganese hydroxide that is primary particles aggregated together. The manganese oxyhydroxide obtained was essentially spherical secondary particles that were primary particles aggregated together, and the average particle size of the secondary particles was 50 μm . Five mols of the above manganese oxyhydroxide were blended with 6 mols of lithium hydroxide, and ion exchanged water was added to this mixture to a total amount of 1 L. This slurry was placed in an autoclave, and hydrothermal processing was performed at a heating process temperature of 200°C and for a heating process duration of 24 hours. The processing conditions of the above process are summarized in Table 1. After the reaction was completed, the slurry was filtrated, washed with water, and dried at 100°C. Subsequent measurement of the X-ray diffraction pattern of the powder obtained confirmed a pattern similar to that of lithium manganese complex oxide. Measurements similar to Example 1 were performed, and the results are shown in Table 2.

[0048]

Example 6

Ten grams of the lithium manganese complex oxide powder obtained in Example 4 were placed in an alumina crucible, and 10 hours of dry heating was performed in an electric furnace, in an air atmosphere at 150°C. The processing conditions of the above process are summarized in Table 1. The powder obtained was a powder free from fusion, and measurement of the X-ray diffraction pattern confirmed a pattern similar to that of lithium manganese complex oxide. Measurements similar to Example 1 were performed, and the results are shown in Table 2.

[0049]

Example 7

Ten grams of the lithium manganese complex oxide powder obtained in Example 1 were placed in an alumina crucible, and 15 hours of dry heating was performed in an electric furnace, in a nitrogen atmosphere at 450°C. The processing conditions of the above process are summarized in Table 1. The powder obtained was a powder free from fusion, and measurement of the X-ray diffraction pattern confirmed a pattern similar to that of lithium manganese complex oxide. Measurements similar to Example 1 were performed, and the results are shown in Table 2.

[0050]

Example 8

A manganese oxyhydroxide (MnOOH) was obtained as in Example 1. The manganese oxyhydroxide obtained was essentially spherical secondary particles that were primary particles aggregated together, and the average particle size of the secondary particles was 10 μm . Three mols of this manganese oxyhydroxide were blended with 6 mols

of lithium hydroxide, and ion exchanged water was added to this mixture to a total amount of 1 L. This slurry was placed in an autoclave, and hydrothermal processing was performed at a heating process temperature of 200°C and for a heating process duration of 4 hours. The processing conditions of the above process are summarized in Table 1. After the reaction was completed, the slurry was filtrated, and then washed with water, and dried at 100°C. Measurement of the X-ray diffraction pattern of the powder obtained confirmed a pattern similar to that of lithium manganese complex oxide. Measurements similar to Example 1 were performed, and the results are shown in Table 2.

[0051]

Example 9

A manganese oxyhydroxide ($\text{Mn}_{0.95}\text{Al}_{0.05}\text{OOH}$) was obtained as in Example 1, except that a carbonate salt of manganese and aluminum blended at a proportion such that the molar ratio will be 0.95 : 0.05 was used. The manganese oxyhydroxide obtained was essentially spherical secondary particles that were primary particles aggregated together, and the average particle size of the granulate particles was 30 μm . Five mols of this manganese oxyhydroxide were blended with 6 mols of lithium hydroxide, and ion exchanged water was added to this mixture to a total amount of 1 L. This slurry was placed in an autoclave, and hydrothermal processing was performed at a heating temperature of 200°C and for a heating process duration of 12 hours. The processing conditions of the above are summarized in Table 1. After the reaction was completed, the slurry was filtrated, washed with water, and dried at 100°C. Subsequent measurement of the X-ray diffraction pattern of the powder obtained confirmed a pattern similar

to that of lithium manganese complex oxide. Measurements similar to Example 1 were performed, and the results are shown in Table 2.

[0052]

Example 10

A manganese oxyhydroxide ($\text{Mn}_{0.95}\text{Cr}_{0.05}\text{OOH}$) was obtained as in Example 1, except that a carbonate salt of manganese and chromium blended at a proportion such that the molar ratio will be 0.95 : 0.05 was used. The manganese oxyhydroxide obtained was essentially spherical secondary particles that were primary particles aggregated together, and the average particle size of the granulate particles was 80 μm . Five mols of this manganese oxyhydroxide were blended with 6 mols of lithium hydroxide, and ion exchanged water was added to this mixture to a total amount of 1 L. This slurry was placed in an autoclave, and hydrothermal processing was performed at a heating temperature of 200°C and for a heating process duration of 12 hours. The processing conditions of the above are summarized in Table 1. After the reaction was completed, the slurry was filtrated, washed with water, and dried at 100°C. Subsequent measurement of the X-ray diffraction pattern of the powder obtained confirmed a pattern similar to that of lithium manganese complex oxide. Measurements similar to Example 1 were performed, and the results are shown in Table 2.

[0053]

Comparative Example 1

(Supplement to The 33rd Denchi Tsuron Kai (Battery Symposium in Japan) (1992), Symposium Proceedings, p. 15 to 16) One mol of commercially available manganese oxyhydroxide and 1 mol of lithium hydroxide were blended in a dry format. The above mixture was placed in an alumina crucible, and 15 hours of a dry calcination process

was performed in an electric furnace, in a nitrogen atmosphere at 450°C. The processing conditions of the above process are summarized in Table 1. Measurement of the X-ray diffraction pattern of the powder obtained showed a pattern of lithium manganese complex oxide, but this powder was a solid mass in which the particles were fused to each other. Measurements similar to Example 1 were performed, and the results are shown in Table 2.

[0054]

Comparative Example 2

Three mols of commercially available manganese oxyhydroxide were blended with 6 mols of lithium hydroxide, and ion exchanged water was added to this mixture to a total amount of 1 L. This slurry was placed in an autoclave, and hydrothermal processing was performed at a heating process temperature of 250°C and for a heating process duration of 4 hours. The processing conditions of the above are summarized in Table 1. After the reaction was completed, the slurry was filtrated, washed with water, and dried at 100°C. Subsequent measurement of the X-ray diffraction pattern of the powder obtained confirmed a pattern similar to that of lithium manganese complex oxide, but the powder was a powdery particle wherein the primary particles did not form secondary particles and existed as discrete particles. Measurements similar to Example 1 were performed, and the results are shown in Table 2.

[0055]

[Table 1]

	Wet heating process				Dry heating process		
	Concentration of manganese oxyhydroxide (mol/l)	Feed of Li/Mn (mol/l)	Temperature of heating process (°C)	Duration of heating process (hours)	Temperature of heating process (°C)	Duration of heating process (hours)	Atmosphere
Ex. 1	0.5	20	100	96	-	-	-
Ex. 2	1	10	120	48	-	-	-
Ex. 3	1	5	150	12	-	-	-
Ex. 4	3	2	200	4	-	-	-
Ex. 5	5	1.2	200	24	-	-	-
Ex. 6	5	1.2	200	12	150	10	Air
Ex. 7	0.5	20	100	96	450	15	Nitrogen
Ex. 8	3	2	200	4	-	-	-
Ex. 9	5	1.2	200	12	-	-	-
Ex. 10	5	1.2	200	12	-	-	-
Com. Ex. 1	-	-	-	-	450	15	Nitrogen
Com. Ex. 2	3	2	250	4	-	-	-

Feed⇒Atomic ratio of raw material

[0056]

[Table 2]

	Shape of particle	Average particle size of primary particles (μm)	Average particle size of secondary particles (μm)	Specific surface area of particles (m ² /g)	X-ray diffraction	State of particle
Ex. 1	Sphere	0.1	2	9	Lithium manganese complex oxide	Good dispersibility
Ex. 2	Sphere	0.1	5	9	Lithium manganese complex oxide	Good dispersibility
Ex. 3	Sphere	0.1	10	8	Lithium manganese complex oxide	Good dispersibility
Ex. 4	Sphere	0.1	10	9	Lithium manganese complex oxide	Good dispersibility
Ex. 5	Sphere	0.2	50	4	Lithium manganese complex oxide	Good dispersibility
Ex. 6	Sphere	0.2	10	6	Lithium manganese complex oxide	Good dispersibility
Ex. 7	Sphere	2	2	0.2	Lithium manganese complex oxide	Good dispersibility
Ex. 8	Sphere	0.1	10	0.2	Lithium manganese complex oxide	Good dispersibility
Ex. 9	Sphere	0.2	30	4	Lithium manganese complex oxide	Good dispersibility
Ex. 10	Sphere	0.2	80	5	Lithium manganese complex oxide	Good dispersibility
Com. Ex. 1	Mass	-	-	5	Lithium manganese complex oxide	Fused solid mass
Com. Ex. 2	Powder	0.3	0.3	7	Lithium manganese complex oxide	-

[0057]

The electron microscope photograph of the lithium manganese complex oxide obtained in Example 6 is shown in Figure 1. The X-ray diffraction chart of the lithium manganese complex oxide obtained in Example 6 is shown in Figure 2. The electron microscope photograph of the lithium manganese complex oxide obtained in Comparative Example 1 is shown in Figure 3.

[0058]

Example 11 Production of Rechargeable Lithium Ion Battery (1)

The lithium manganese complex oxide obtained in Example 6, acetylene black, and Teflon were kneaded well at a ratio by weight of 87 : 6.5 : 6.5, coated evenly on a clean stainless steel mesh (20 mm ϕ), and then pressed together at 200 kg/cm², and dried for approximately 17 hours under reduced pressure at 150°C, to produce a positive electrode. A metal lithium foil (20 mm ϕ , thickness of 0.2 mm) was used as the negative electrode, and a nonwoven fabric and a polypropylene microfilm were used as separators. The electrolyte used was a mixture of a 1 M solution of LiClO₄ in propylene carbonate and 1,2-dimethoxyethane (1 : 1), wherein the water content was 20 ppm or less, and the separator was soaked in the mixture. These components were incorporated in the battery shown in Figure 4.

[0059]

Using the battery produced from the above method, charge and discharge was repeated at a constant current of 0.2 mA/cm² and the battery voltage between 4.3 and 2.0 V. The density of the positive active material of this positive electrode material film, the discharge capacity per unit volume after the third charge and discharge cycle, and the discharge capacity per unit weight are shown in Table 3.

[0060]

Example 12 Production of Rechargeable Lithium Ion Battery (2)

A rechargeable battery was produced as in Example 11, except that the lithium manganese complex oxide obtained in Example 8 was used. Using the battery produced, charge and discharge was repeated at a constant current of 0.2 mA/cm^2 and the battery voltage between 4.3 and 2.0 V. The results are shown in Table 3.

[0061]

Comparative Example 3 Production of Rechargeable Lithium Ion Battery (3)

A rechargeable battery was produced as in Example 11, except that the lithium manganese complex oxide obtained in Comparative Example 1 was used. Using the battery produced, charge and discharge was repeated at a constant current of 0.2 mA/cm^2 and the battery voltage between 4.3 and 2.0 V. The results are shown in Table 3.

[0062]

Comparative Example 4 Production of Rechargeable Lithium Ion Battery (4)

A rechargeable battery was produced as in Example 11, except that the lithium manganese complex oxide obtained in Comparative Example 2 was used. Using the battery produced, charge and discharge was repeated at a constant current of 0.2 mA/cm^2 and the battery voltage between 4.3 and 2.0 V. The results are shown in Table 3.

[0063]

[Table 3]

	Density of active material of positive electrode material in the film of positive electrode material (g/cm^3)	Discharge capacity per unit volume after third cycle (mAh/cm^3)	Discharge capacity per unit weight after third cycle (mAh/g)
Ex. 11	1.7	320	190
Ex. 12	1.7	330	195
Com. Ex. 3	1.5	230	150
Com. Ex. 4	1.2	230	195

[0064]

[Advantages of the Invention]

With the present invention described above, particulate composition can be efficiently obtained that has narrow particle size distribution, large specific surface area, and homogeneous composition, as well as that can be used favorably as a positive active material of a rechargeable lithium ion battery. Moreover, in a rechargeable lithium ion battery that uses the particulate composition of the present invention as the positive active material, a large amount of electrical quantity can be retrieved, and it can be used favorably in for example electronic and medical equipments. The present invention achieves unique effects by virtue of applying a hydrothermal method instead of calcination.

[Brief Description of the Drawings]

[Figure 1]

The electron microscope photograph of the particulate composition from Example 6.

[Figure 2]

The X-ray diffraction chart of the particulate composition from Example 6. The vertical axis represents the intensity of X-ray (cps), and the horizontal axis represents the diffraction angle (2θ).

[Figure 3]

The electron microscope photograph of the massive particle obtained in Comparative Example 1.

[Figure 4]

The sectional view showing the configuration of the rechargeable lithium ion battery from Example 11.

[Description of Symbols]

- 1 Lead wire
- 2 Collector mesh for positive electrode
- 3 Positive electrode
- 4 Separator
- 5 Negative electrode
- 6 Collector mesh for negative electrode